

# MICROHETEROGENEITY OF SOLVENT-SWOLLEN COAL PROBED BY PROTON SPIN DIFFUSION

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## ABSTRACT

Phase separated structure of solvent swollen coal was characterized through its property of proton flip-flop spin diffusion. It is shown that the fashion of coal swelling is non-uniform on a segmental scale and a microscopic phase separation does take place on a scale from several to 20 nm even in good solvents like pyridine.

## INTRODUCTION

The most convincing model of coal structure is that of a cross-linked macromolecular network. All attempts to relate the macromolecular network parameters such as the molecular weight between cross-link points to the degree of swelling in a good solvent have taken the Flory-Rehner theory <sup>1</sup> as a starting point for the swelling of macromolecular networks. The theory involves the assumption that the deformation is affine, i.e., that the primitive chain is deformed in the same way as the macroscopic deformation (swelling) of the sample. Accordingly, the premise is required that the swollen coal is uniform in the segmental scale when we relate the macroscopic swelling to the molecular characteristics such as cross-link density. Based on the <sup>1</sup>H NMR transverse relaxation characteristics, however, it was found that the hydrogens in pyridine-swollen coals could be divided into two groups: those whose relaxation was characteristic of solids and those whose relaxation was characteristic of liquids. Barton et al. <sup>2</sup> reported that the <sup>1</sup>H NMR transverse relaxation signals measured at ambient temperature for bituminous coals swollen by deuterated pyridine, show that up to ~60% of the coal molecular structures can be sufficiently destabilized to become mobile. Therefore, at least 40% of the coal hydrogen remains in rigid molecular structures and is characterized by an NMR signal component that is similar to the signal for the corresponding dry coal. This result demonstrates that the swollen coal can be recognized to have a phase separated structure involving solvent rich phase and apparently solvent impervious phase. However the scale of heterogeneity in the swollen coals is presently not fully understood.

In spite of its indirect character, measurements of <sup>1</sup>H spin diffusion by pulsed NMR have proven to be a useful technique for evaluating the compatibility of polymer blends <sup>3-6</sup> and the microdomain structure of multiphase polymers. <sup>7-11</sup> When a nuclear system is disarranged from equilibrium in an NMR experiment, the excess spin energy acquired by the resonant nuclei can remain in the spin system for a long time compared to transverse relaxation time,  $T_2$ , before being transferred to the lattice. This follows directly from the fact that longitudinal relaxation time,  $T_1$ , is much larger than  $T_2$  in solid materials. <sup>12</sup> During this time the spin energy can disperse between neighboring nuclei by energy-conserving "flip-flop" spin transitions. This process is termed spin diffusion and may provide observable energy transport over distances of several tens of nanometers. For the coal swollen by the saturation of deuterated pyridine, there exists at least two distinct morphological regions in the NMR sense. In such a case, owing to their state of motion, certain regions or sites responsible for the mobile phase provide exceptionally efficient transfer of energy to the lattice, while the rigid component weakly coupled to the lattice, can exhibit molecular motions that disfavor relaxation. It is possible, through the mechanism of spin diffusion, for the component that is tightly coupled to the lattice to relax other resonant nuclei in the spin system either totally or partially. By analyzing the spin diffusion process under an appropriate initial and boundary conditions, we can estimate the diffusive path length, and then get an information about the domain size of each phase.

In this study, the phase separated structure of solvent swollen coal is characterized through its property of proton flip-flop spin diffusion. Six coals of different rank swollen by the saturation of deuterated pyridine were subjected to <sup>1</sup>H NMR relaxation measurements. The NMR experiments provide transverse relaxation time,  $T_2$ , longitudinal relaxation time,  $T_1$ , and that in the rotating frame  $T_{1\rho}$ . The time dependency of the spin diffusion is also monitored by Goldman-Shen pulse sequence. The dimension of a heterogeneity of the swollen coal is evaluated by analyzing the spin diffusion process.

## EXPERIMENTAL

**Samples.** Four Argonne Premium Coal Sample Program (PCSP) coals <sup>13</sup> and a brown coal were used as coal samples. Their particle sizes were finer than 150  $\mu$ m. They were dried under a pressure of less than 1 Pa at 333 K for 48 h, which is long enough to attain a constant weight. The elemental composition, ash and water contents, and swelling ratios of the coal samples in pyridine or pyridine/CS<sub>2</sub> mixed solvent are listed in Table 1. The coal sample was weighed and transferred to an NMR tube with a 10 mm o.d. The mass of the sample was 0.3 g. A 0.5 g of fully deuterated pyridine, Py-d<sub>5</sub>, (Aldrich, 99.99% atom D) was

then added to the sample and the tube was sealed under pressure of less than 2 Pa while frozen with liquid nitrogen. A mixture of Py- $d_6$  and CS<sub>2</sub> (1:1 by volume) was also used as a solvent for UF coal. The coal-solvent mixtures were stored at 303 K for at least 4 months before the NMR measurement. Styrene/divinylbenzene copolymers (St/DVB, crosslink density, 2, 4, and 8%) swollen in benzene- $d_6$  were also prepared.

**<sup>1</sup>H NMR.** NMR measurements were carried out at 303 K using JEOL Mu-25 NMR spectrometer equipped with spin locking unit operating at a proton resonance frequency of 25 MHz. The solid-echo pulse sequence, 90°- $\tau$ -90° (90° phase shift) provided an approximation to the complete free induction decay (FID). Typical values for the pulse width, pulse spacing, repetition time and number of scans were 2.0  $\mu$ s, 8.0  $\mu$ s, 6 s and 32, respectively. The saturation recovery pulse sequence, 90°- $\tau$ -90°, was used to monitor the recovery of the magnetization with the pulse separation time,  $t$  and provided  $T_1$ .  $T_{1\rho}$  was measured by the so-called spin-locking pulse sequence, that is 90° pulse is followed by a reduced amplitude pulse, sustained for a time  $t$  and phase shifted 90°. The magnetization remaining at time  $t$  is monitored by observation of the free induction signal. Rotating frame measurements were made at radiofrequency field of 6 G. Spin diffusion was monitored by the Goldman-Shen pulse sequence.<sup>14</sup> The original pulse sequence was modified as 90°- $\tau$ -90°- $\tau$ -90°- $\tau$ -90°, according to Tanaka and Nishi<sup>11</sup> in order to avoid the dead-time effect after the pulse.

## RESULTS AND DISCUSSION

**Transverse relaxation characteristics.** The natural logarithm of the FID curves for the dried and swollen YL coal are drawn as a function of decay time in Figure 1(a). Although the solvent swelling enhance the fraction of slowly decaying components, a portion of coal hydrogen remains rigid. The observed FID was assumed to be expressed by the following equations and numerically analyzed by nonlinear least squares methods.

$$I(t) = I_G(0) \exp[-t^2/2T_{2G}^2] + I_{L1}(0) \exp[-t/T_{2L1}] + I_{L2}(0) \exp[-t/T_{2L2}] \quad (1)$$

where  $I(t)$  and  $I_i(t)$  are the observed intensity at time  $t$ , and that attributed to component  $i$ , respectively, and  $T_{2i}$  is the transverse relaxation time of the  $i$ th component. The fraction of hydrogen producing exponential decays,  $H_m$ , are listed in Table 2.  $H_m$  for the swollen coal samples range from 0.2 to 0.6, and  $T_{2G}$  value is similar to that for the corresponding dry coal. In contrast, when exposed to benzene- $d_6$ , hydrogens in St/DVB crosslinked copolymer are entirely converted to mobile hydrogens producing exponential decays, regardless of cross link densities of St/DVB as illustrating in Figure 1(b). This indicates that solvent penetrates thoroughly into St/DVB and it is likely to be deformed in a more or less uniform fashion. For the swollen coal samples, it is clear that there are domains which do not swell and are not penetrated by solvent as shown schematically in Figure 2. The phase structures of the swollen coal are separated into at least two phase, i.e., solvent rich (SR) and solvent impervious phase (SI). Brenner<sup>15</sup> studied the changes in optical anisotropy of dry and solvent-swollen thin section samples of a bituminous coal. He found that the natural optical anisotropy was completely relaxed by immersion of the coal in pyridine. These different experimental techniques, i.e., <sup>1</sup>H NMR and optical microscopy, produce different conclusion on the phase structure in the solvent-swollen coal. This contradiction seems to be responsible for the difference in the spatial resolution between these experimental techniques. The optical microscopy technique can hardly detect heterogeneities whose spatial dimensions are less than the optical wavelength (400–700 nm). Therefore, the dimension of heterogeneities of the swollen coal must be smaller than ~700 nm.

**Longitudinal relaxation characteristics and spin diffusion.** To examine whether the spin diffusion process is active or not in the swollen coal samples, proton longitudinal relaxation was measured both in the laboratory and rotating frame. Figure 3(a) shows the result of  $T_1$  measurement for the swollen UF coal.  $T_1$  is almost composed of one component while  $T_{1\rho}$  can be analyzed by the sum of two exponential functions as shown in Figure 3(b). From these results, one can clearly understand the effect of spin diffusion.  $T_2$  signals are composed of three components without the effect of spin diffusion while  $T_{1\rho}$  and  $T_1$  measurements are affected strongly by spin diffusion and the number of the components decreases from  $T_{1\rho}$  to  $T_1$ . The existence of at least two time constants for a rotating frame longitudinal relaxation process i.e.,  $T_{1\rho}$ , in a system means that spin-diffusion processes cannot effectively average the different dynamical properties of protons in different spatial domains on the relevant time scale of the specific relaxation process. On the other hand, in the time scale of  $T_1$  measurements, the distinctly separated spin systems were sufficiently averaged by the spin diffusion. The scale of spatial heterogeneities of the swollen coals can be estimated by evaluating the diffusive path length,  $L$ , i.e., the maximum linear scale over which diffusion is effective. The approximate expression is

$$L = (2dDt)^{1/2} \quad (2)$$

where  $d$  is spatial dimension, i.e., the degree of freedom of diffusion,  $D$  is diffusion coefficient, and  $t$  is characteristic time for diffusion.  $d$  is one, two, and three corresponds to the domain shape of lamella, cylinder and sphere, respectively. It has been shown that in a regular lattice with lattice constant  $a$ , the spin diffusion coefficient due to dipolar spin flip is given

by<sup>8</sup>

$$D = 0.13 a^2 \sqrt{M_2} \quad (3)$$

where  $M_2$  is the second moment of the NMR line shape. For both Gaussian and Lorentzian line shapes,  $\sqrt{M_2} = T_2^{-1}$ . For a regular lattice,  $D$  can be principally calculated from eq 3, but since the lattice constant is an ill-defined quantity for disordered materials like coals, a theoretical value can only be estimated by

$$D \approx 0.13 \bar{a}^2 / T_{2g} \quad (4)$$

where  $\bar{a}^2$  is the average of the square of distances between adjacent protons in the solvent impervious domain. Because of the lack of information on the molecular structure of coal, it is impossible to accurately determine  $\bar{a}^2$ . However,  $\bar{a}^2$  of the coal samples can be estimated semiquantitatively from the data of true densities evaluated by helium pycnometry<sup>16</sup> and hydrogen contents of the corresponding dry coal<sup>13</sup> by assuming a cubic lattice of hydrogens. In Table 2, the estimated values of  $D$  are listed.  $D$  range from  $5.1 \times 10^{-12}$  to  $6.2 \times 10^{-12}$  cm<sup>2</sup>/s and have the same order in many organic polymer systems. The observed longitudinal relaxation time corresponds to the characteristic time  $t$ . By assuming  $d$  is 3, we can estimate  $L$  as 40 nm from eq 2 for UF/Py- $d_5$ . Therefore the linear dimension of the structural heterogeneity in UF/Py- $d_5$  is certainly less than 40 nm on the basis of  $T_1$  data. Following the same procedure for the  $T_{1\rho}$  data the lower limits of the heterogeneity can be estimated to be 1 nm from the short  $T_{1\rho}$ . For UF/(Py- $d_5$  + CS<sub>2</sub>), the limiting size in heterogeneity can be estimated as 1 - 20 nm. Recently, Xiong and Maciel<sup>17</sup> studied the proton longitudinal relaxation characteristics in dry coal using a solid state high resolution NMR technique. They found two  $T_{1\rho}$  values for the three kind of bituminous coals, which indicates the existence of structural heterogeneity in the coals on a spatial scale of at least of 5 nm. While these estimates are crude they nevertheless provide some information of the maximum diffusive path lengths probed by the NMR experiment when spin diffusion is operative. The Goldman-Shen pulse sequence was thus employed to monitor the spin diffusion process. The advantage of the Goldman-Shen experiment is that the time for spin diffusion can be arbitrarily varied, and if this time is much less than  $T_1$ , the analysis is straightforward.

**Goldman-Shen experiment.** The Goldman-Shen experiment is a technique to put the separate spin systems at different spin temperatures and then sample them as a function of time so that their approach to equilibrium can be followed. The modified Goldman-Shen pulse sequence used in this experiment is shown in Figure 4. During time  $\tau_0$ , the magnetization in the SI phase has decayed to zero, while there is still sufficient magnetization in the SR phase. During the pulse interval  $t$ , spin diffusion through the magnetic dipolar coupling occurs from the SR phase to the SI one. The third 90° pulse rotates the magnetization into the transverse plane for observation and the final 90° pulse creates the solid echo. The typical decaying signals after the Goldman-Shen pulse sequence observed in IL/Py- $d_5$  for various values of the pulse interval  $t$  are shown in Figure 5. The recovery of the fast decaying component is observed. The recovery factor,  $R(t)$ , of the magnetization of SI phase can be defined as

$$R(t) = \frac{M(t) - M(t \rightarrow 0)}{M(t \rightarrow \infty) - M(t \rightarrow 0)} \quad (5)$$

In Figure 6,  $R(t)$  is plotted versus  $\tau^{1/2}$  for the solvent-swollen BZ and PT coal. The time evolution of  $R(t)$  is analyzed by the diffusion equation solved by Cheung and Gerstain<sup>8</sup> to get information on the domain size. The transfer of the magnetization in solids via dipolar spin flip interaction may be described by the spin diffusion equation

$$\frac{\partial}{\partial t} m(r, t) = D \nabla^2 m(r, t) \quad (6)$$

where  $m(r, t)$  is the local magnetization density at site  $r$  and time  $t$ . The differential equation is then solved according to the appropriate boundary and initial conditions. The analytical solution of eq 6 due to Cheung and Gerstain is

$$R(t) = 1 - \varphi_x(t) \varphi_y(t) \varphi_z(t) \\ \varphi_a(t) = \exp(Dt/\bar{b}^2) \operatorname{erfc}(Dt/\bar{b}^2)^{1/2} \text{ for } a = x, y, z \quad (7)$$

where  $\bar{b}$  is the mean width of domains in SR phase. The quantity  $(D/\bar{b}^2)$  was considered as an adjustable parameter. The solid curves in Figure 6 represent the nonlinear least squares fits to the data by using eq 7. The results for the analytical fits are listed in Table 2. These calculations indicate that the SR phase domain in the swollen coals have sizes ranging from several to 20 nm. The size seems to become smaller with decreasing coal

rank. The information on the morphologies of the domains is necessary to estimate the domain size adequately. However there is presently little information available on the shape of domains in the swollen coal.  $\bar{b}$  is the mean width of domains in SR phase and would corresponds to the distance between the domains in SI phase. Cody and Thiagarajan<sup>18</sup> estimated the interdomain spacing of a pyridine-swollen bituminous coal to be approximately 15 nm by the small angle neutron scattering technique. This value agrees well  $\bar{b}$  of the swollen bituminous coals, i.e., IL, PT, and UF coals, which were evaluated under the assumptions that the domain shapes are cylinder or sphere.

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**Table 1 Properties of Coal Samples.**

Coal	(Symbol)	C	H	N	S	O <sup>a</sup>	ash	Swelling ratio <sup>d</sup>	
		[wt% daf <sup>b</sup> coal]					[wt% mf <sup>c</sup> coal]	Py[-]	Py/CS <sub>2</sub> [-]
Yallourn	(YL)	65.0	4.6	0.6	0.2	29.6	57.5	2.7	
Beulah Zap	(BZ)	72.9	4.8	1.2	0.7	20.3	32.2	2.2	2.0
Illinois#6	(IL)	77.7	5.0	1.4	2.4	13.5	8.0	2.8	
Pittsburgh	(PT)	83.2	5.3	1.6	0.9	8.8	9.3	2.4	
Upper Freeport	(UF)	85.5	4.7	1.6	0.7	7.5	13.2	1.0	1.9

<sup>a</sup> by difference. <sup>b</sup> dry-ash-free. <sup>c</sup> moisture-free. <sup>d</sup> determined by the method proposed by Green et al.

**Table 2 Domain Size of Solvent Rich Phase.**

Sample	Solvent	SC <sup>a</sup>	H <sub>m</sub> <sup>b</sup> [-]	D[10 <sup>-12</sup> cm <sup>2</sup> /s]	1-D	$\bar{b}$ [nm]	3-D
						2-D	
YL	py	1.75	0.56	-	-	-	-
YL	py	3.50	0.60	5.7	2	5	8
BZ	py	1.75	0.44	6.2	2	5	8
BZ	py/CS <sub>2</sub>	1.81	0.34	-	-	-	-
IL	py	1.75	0.55	5.6	5	12	19
PT	py	1.75	0.51	5.5	5	12	21
UF	py	1.75	0.20	-	-	-	-
UF	py/CS <sub>2</sub>	1.81	0.45	5.1	5	10	16
St/2%DVB	benz	4.75	1.00	-	-	-	-
St/4%DVB	benz	2.31	1.00	-	-	-	-
St/8%DVB	benz	2.31	1.00	-	-	-	-

<sup>a</sup> Mass ratio of solvent to coal or polymer. <sup>b</sup> Fraction of mobile hydrogen producing exponential decays.

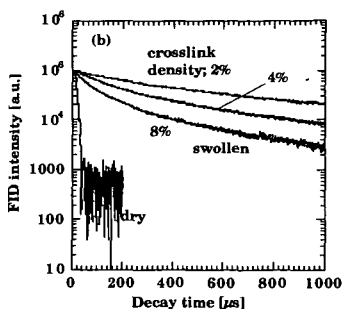
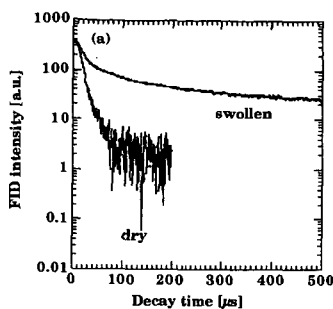


Figure 1  $^1\text{H}$ -NMR transverse relaxation signals. (a) dried and swollen YL (pyridine- $d_5$ ,  $S/C=1.75$ ), (b) dried and swollen St/DVB. (benzene- $d_6$ ,  $S/C=2.31$  for 4% and 8% crosslink densities,  $S/C=4.75$  for 2%)

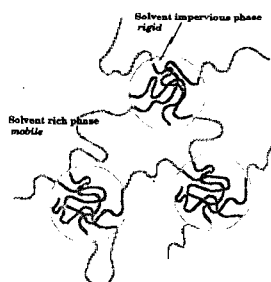


Figure 2 Conceptual model for microdomain structure of solvent-swollen coal.

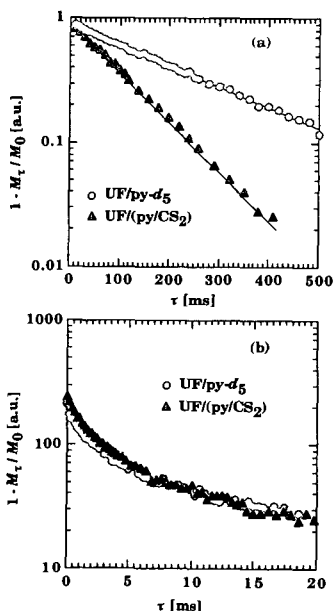


Figure 3  $T_1$  and  $T_{1\rho}$  plots for solvent-swollen UF. (a)  $T_1$ , (b)  $T_{1\rho}$

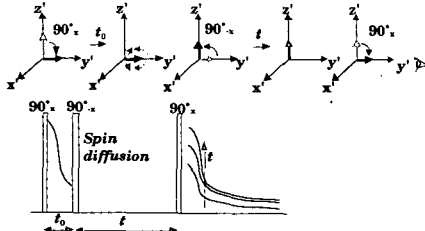


Figure 4 Schematic figure of the Goldman-Shen pulse sequence.

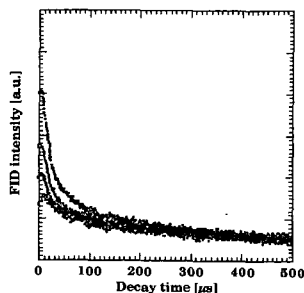


Figure 5 Solid-echo signals of swollen YL (pyridine- $d_5$ ,  $S/C=1.75$ ) after the modified Goldman-Shen pulse sequence for various value of  $t$ .  $t$  is equal to 1, 25, 64 and 225 ms from the bottom

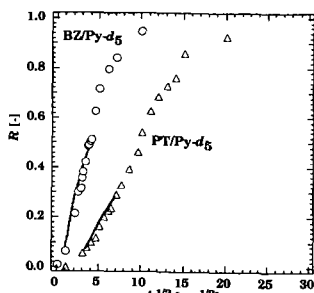


Figure 6 Recovery of proton magnetization in SI phase as a function of  $t^{1/2}$  for the solvent-swollen BZ and PT coal. Solid lines represent the best fit to the data by using eq 7.